PB83-220236

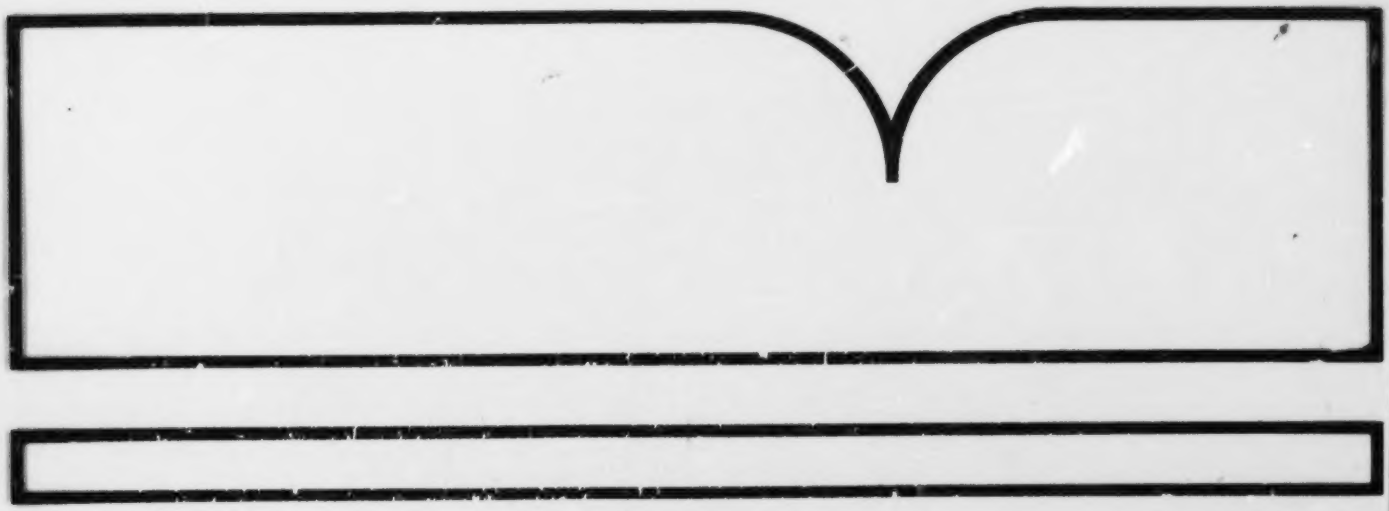
Performance Audit Program for Gaseous Certified Reference Materials

Research Triangle Inst.
Research Triangle Park, NC

Prepared for

Environmental Monitoring Systems Lab.
Research Triangle Park, NC

Jun 83



U.S. Department of Commerce
National Technical Information Service
NTIS

PB83-220236

EPA-600/D-83-059
June 1983

THE PERFORMANCE AUDIT PROGRAM FOR GASEOUS CERTIFIED REFERENCE MATERIALS

Robert S. Wright
W. Cary Eaton
Clifford E. Decker

Research Triangle Institute
Research Triangle Park, North Carolina

Darryl J. von Lehmden

U.S. Environmental Protection Agency
Research Triangle Park, North Carolina

For Presentation at The 76th Annual Meeting of

the Air Pollution Control Association

Atlanta, Georgia June 19 to 24, 1983

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/D-83-059		PB83 220236

4. TITLE AND SUBTITLE	5. REPORT DATE
The Performance Audit Program for Gaseous Certified Reference Materials	June 1983
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
R.S. Wright, W.C. Eaton, C.E. Decker, Research Triangle Institute and D.J. von Lehmden, U.S. EPA	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Research Triangle Institute Research Triangle Park, North Carolina 27709	DU No A119, Project E0102
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	14. SPONSORING AGENCY CODE EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

In the past, Environmental Protection Agency (EPA) regulations have required that gaseous pollutant calibration standards for ambient air and mobile source emission measurements be traceable to National Bureau of Standards (NBS) Standard Reference Materials (SRMs) or other approved gases. Recently, these regulations have been amended or interpreted to allow the calibration standards to be traceable either to SRMs or to Certified Reference Materials (CRMs) which may be purchased from specialty gas vendors. Traceability to either SRMs or CRMs will also be required in new regulations which are being developed for stationary source emission measurements. The purpose of this paper is to discuss EPA's performance audit program for CRMs. This program is part of a comprehensive quality assurance effort which permits CRMs to be considered as essentially equivalent to SRMs.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Certified Reference Materials(CRM), Standard Reference Materials (SRM), traceability, performances. audit, regulations		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
	Unclassified	17
Release to Public	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

THE PERFORMANCE AUDIT PROGRAM FOR GASEOUS CERTIFIED REFERENCE MATERIALS

Introduction

The legal and economic implications of ambient air quality and source emission measurements demand that accurate and stable standards be used to calibrate the monitoring instrumentation. In the past, Environmental Protection Agency (EPA) regulations have required that gaseous pollutant calibration standards for ambient air quality measurements be traceable to National Bureau of Standards (NBS) Standard Reference Materials (SRMs) (1). Similarly, calibration standards for mobile source emission measurements are required to be traceable to either NBS SRMs or other gas standards which have been approved by EPA's Administrator (2). SRMs were developed to provide more accurate calibration standards than were available from commercial sources at the time (3). As a result of their acceptance as benchmarks for air pollution measurements, the demand for SRMs occasionally exceeds the ability of NBS to produce them and at times NBS's inventory of certain SRMs has been exhausted. In response to this demand, NBS and EPA have established a procedure by which specialty gas vendors may produce a new type of standard, Certified Reference Materials (CRMs), which have essentially the same accuracy as SRMs (4,5). Recently, EPA regulations have been amended or interpreted to allow calibration standards to be traceable to either SRMs or CRMs (6,7). Traceability to either SRMs or CRMs will also be required in new regulations being developed for stationary source emission measurements.

As of the winter of 1983, the specialty gas vendors had produced CRMs containing carbon monoxide in nitrogen, carbon monoxide in air or nitric oxide in nitrogen. Additionally, NBS has established procedures for the production of CRMs that contain sulfur dioxide in nitrogen, propane in nitrogen, or propane in air. A procedure for the production of carbon dioxide in nitrogen CRMs is under development at NBS. EPA maintains a list of all batches of CRMs that have been approved for sale (8).

Quality Assurance for Certified Reference Materials

If CRMs are to be accepted as substitutes for SRMs, they must meet three criteria: they must be available in sufficient quantities to satisfy the demand, their price must be competitive with that of SRMs, and they must be credible standards having a small and well-defined uncertainty. While the establishment of the first two criteria is properly in the vendors' province, responsibility for establishing the credibility of CRMs is jointly shared by the vendors, by NBS, and by EPA. EPA and NBS have established a comprehensive quality assurance (QA) program for CRMs involving all aspects of their production and analysis. The program consists of the following elements.

1. A CRM batch is closely linked to an existing SRM. The batch is produced so that its concentration lies within ± 1 percent relative of the concentration of the SRM. Because this SRM is also used as the reference standard for both the analysis and the performance audit of the batch, comparison of the two sets of measurements is valid. In general, this link gives the CRM batch essentially the same accuracy as the SRM.

2. Each CRM batch consists of at least 10 cylinders with identical concentrations. The batch must be large enough to allow valid statistical inferences to be drawn concerning the homogeneity of the batch and the concentration of individual cylinders in the batch.

3. The vendor performs two analyses of a CRM batch separated by a 1- or 2-month "incubation" period. These analyses permit the stability of the batch to be evaluated.

4. A blind performance audit of random samples from the batch is conducted at an EPA-chosen laboratory. This audit provides NBS with an independent assessment of the CRM batch's concentration.

5. Both the vendor's and the auditor's analytical results are reviewed throughly by NBS before the batch is approved for sale. These results must demonstrate that the batch is stable and homogeneous and that the batch's concentration has been measured accurately.

6. Individual CRMs have a 2-year certification period. The limited certification period reduces the chance that CRMs that have decayed over long periods will be used.

7. A purchaser of a CRM is supplied with an individual certificate of analysis for the particular cylinder and NBS documentation concerning the vendor's and auditor's analytical results for the entire batch. The certificate and documentation assure the purchaser that the CRM was prepared according to the official procedure and that auditor's results and the NBS review confirm the vendor's results.

In addition to these seven elements, a vendor batch recertification and recordkeeping program is under development at NBS and EPA. This program will consist of periodic long-term stability checks of the unsold CRMs in a batch and a procedure for notifying purchasers of CRMs if instabilities in the CRMS are detected. These QA elements allow the long-term certification of the unsold portions of a batch.

The purpose of this paper is to discuss the fourth element in this overall QA program, EPA's performance audit program for CRMs. The performance audits are being conducted at the Research Triangle Institute (RTI) in Research Triangle Park, North Carolina under EPA Contract No. 68-02-3431.

The Performance Audit Program

The purpose of the EPA performance audit program is to provide NBS with an independent set of analytical data on a vendor-produced batch of CRMs. A performance audit is conducted on two samples from the batch by analysis at an independent laboratory chosen and funded by EPA (in this case, RTI). If NBS finds that the auditor's analytical data confirms the vendor's analytical data for the two samples then NBS can conclude that the vendor has accurately measured the two samples and, by inference, the remainder of the batch.

The audit procedure begins after a vendor has produced a CRM batch and is satisfied that the batch is stable and homogeneous At the same time that the vendor sends a report of its analytical results to NBS, the vendor notifies the auditor that a CRM batch is available to be audited. The auditor then selects two random samples from the batch and requests that the vendor send the samples to be audited. The only information that the auditor receives about the batch is the sample number and stamped cylinder number for each cylinder in the batch. The auditor is not informed of the vendor's analytical results. Thus, the auditor cannot subjectively interpret audit data based on prior knowledge of the vendor's analytical results.

The general features of the subsequent audit have been specified by NBS but the details have been left to the discretion of the auditor. The auditor is required to make at least 10 distinct and precise measurements of each sample. The reference standard for the measurements must be an SRM having the same nominal concentration as the samples. Measurement of additional SRMs having different concentrations is required to demonstrate the linearity of the instrument used to measure the samples. When the audit has been completed, the auditor reports to NBS the individual measurements for each sample and their averages and standard deviations. If the standard deviations of these audit measurements exceed 0.5 percent relative, the audit must be repeated.

The detailed audit procedures and analytical methods in use at RTI were adapted from those used by NBS in its analyses of SRMs (9). Conventional ambient air or source emission monitoring instruments (e.g., nondispersive infrared for carbon monoxide and chemiluminescence for nitric oxide) are used to measure the CRMs and the reference standards. All measurements are made on undiluted sample gas. Averaging multiple voltage readings of a continuously flowing sample stream with a data logger produces a value that is more precise than a single voltage readings. A strip chart recorder is used to verify that the instrument's response is stable prior to the start of data collection. A low-pressure sampling manifold is used to control which CRM or reference standard is being measured at any given moment. Each cylinder is plumbed to the manifold via a pressure regulator, a fine metering valve, and a solenoid valve, which is sequentially actuated by an electronic power-switching digital timer.

The three instrumental sources of uncertainty that may affect the precision of the CRM audit are short-term noise and long-term zero and sensitivity drifts. The uncertainty due to noise is reduced by the use of average voltages rather than instantaneous voltages. The uncertainty due to zero and sensitivity drifts is reduced by frequent measurement of a zero gas and the SRM reference standard. The measurement cycle used for CRM audits is Zero-SRM-CRM(1)-CRM(2) as shown in Figure 1. This cycle is repeated 10 or more times during a CRM audit. Each set of CRM measurements is preceded and followed by zero gas and SRM measurements. Zero corrections and sensitivities for each CRM measurement are calculated by interpolation between the calibration standard measurements.

In its report to NBS, the auditor provides the data from the CRM measurements and from the linearity check. Additional information concerning the analytical instrumentation, the analytical procedures, and the reference standards is also reported. NBS reviews the auditor's report and compares it with the vendor's analytical report. Three criteria must be satisfied before NBS will notify the vendor that the batch may be certified for sale as CRMs. First, the vendor's analytical data must demonstrate that the batch is stable and homogeneous. Second, the batch's concentration must be within $\pm$ 1 percent relative of the SRM's concentration. Third, there must be no significant difference between the vendor's and the auditor's analytical results.

In the event that a significant difference exists between the two sets of results, the two samples batch are sent to NBS for a definitive analysis. NBS may also request that the vendor perform additional analyses of the batch if there are unresolved questions. Thus, NBS remains the final arbitrator concerning the homogeneity, stability, and accuracy of these standards. The active participation of NBS in the production of CRMs ensures their credibility.

Example Vendor and Auditor Analytical Results

Vendor and auditor results that were obtained for a batch of 47.2 ppm carbon monoxide in nitrogen CRMs can be used to illustrate the NBS review process. This batch was produced to duplicate an SRM containing 47.1 ppm carbon monoxide in nitrogen. Table I gives the vendor's results. Sample 1 is the internal standard for the batch, which means that its concentration was determined by direct comparison with the SRM. The internal standard was, in turn, used as the reference standard during the measurements of the remainder of the batch. NBS determined that the batch was homogeneous because the standard deviation of each batch analysis was reasonably close to the standard deviation of the corresponding internal standard analysis (e.g., a standard deviation of 0.137 ppm for the first analysis of the batch is reasonably close to a standard deviation of 0.076 ppm for the first analysis of the internal standard). NBS determined that the batch was stable by comparing the difference in concentration between the first and second analyses for each cylinder in the batch. The "paired difference test" indicated that these differences were not statistically significant.

It should also be noted that the overall average batch concentration (i.e., 47.177 ppm) was well within 1 percent relative of the SRM's concentration.

RTI randomly chose samples 5 and 7 from the batch to be audited. The audit's mean measured concentrations for samples 5 and 7 (see Table II) were within 0.18 percent relative of the mean concentrations determined by the vendor. A total batch uncertainty of 0.276 ppm was calculated from the vendor's analytical results. This value includes the uncertainties in the measurement of the CRMs and the internal standard and the uncertainty in the certified value of the SRM. The corresponding total uncertainty for the auditor's analytical results was 0.245 ppm. Based on these total uncertainties, NBS concluded that there was no significant difference between the two sets of results. Because the three criteria mentioned above had been met, NBS notified the vendor that the batch could be certified for sale as CRMs.

Evaluation of Auditor Performance by NBS

Prior to the vendors' beginning the production of a particular class of CRMs, NBS evaluates RTI's ability to perform audits of this class by sending "unknowns" to RTI for analysis. These unknowns are SRMs from NBS's inventory whose concentrations are unknown to RTI. They are analyzed in the same manner as samples from a CRM batch. There must be reasonably close agreement between RTI's results and the certified values for these SRMs. As of the winter of 1983, analyses had been conducted for 14 unknowns containing carbon monoxide in nitrogen, nitric oxide in nitrogen, or sulfur dioxide in nitrogen. The results of these analyses are summarized in Table III. A histogram showing the frequency distribution of the agreement between the NBS-certified value and the RTI-measured value is given in Figure 2. In general, the agreement has been within 0.5 percent relative. The level of agreement attained during analyses of the unknowns demonstrates the ability of an independent laboratory to measure gaseous calibration standards with a high degree of accuracy. This knowledge has allowed EPA and NBS to proceed in implementing the CRM performance audit program.

Results of Audits of CRM Batches

Through the winter of 1983, performance audits were performed on samples from 26 batches of CRMs containing carbon monoxide in nitrogen, carbon monoxide in air, or nitric oxide in nitrogen. NBS notified vendors that 23 of these batches could be certified for sale as CRMs. The certification of the 3 remaining batches has been delayed pending further analyses by the vendors even though acceptable agreement was obtained between the vendor's and the auditor's results. Table IV summarizes the results for the 23 batches approved for sale. This table compares the auditor's results with the vendor's results and shows the agreement between each pair of results. In general, the

agreement has been within 0.5 percent relative as shown in Figure 3. The average agreement for the 46 samples is 0.19 percent relative and the largest value is 0.61 percent relative. For two of the approved batches, NBS conducted definitive analyses of the audited samples. In both cases, very close agreement was found between the results obtained by RTI and those obtained by NBS.

Long-Term Stability of CRMs

One feature essential to the credibility of NBS-SRMs is their certified long-term stability. Generally, the concentration listed on an SRM's certificate is valid for 2 years following its sale. Research at NBS has demonstrated the stability of gaseous SRMs as a general class (3). Additionally, NBS conducts periodic long-term stability checks on representative samples from each batch of SRMs. If significant changes are detected in a batch's concentration during the 2-year period, NBS notifies the purchasers of SRMs from that batch.

Establishment of a similar record of long-term stability for CRMs is needed but will necessarily take time. The vendor batch recertification and recordkeeping program that is under development will include a procedure for making long-term stability measurements.

As an interim measure, an informal long-term stability study has been conducted with the cooperation of the vendors. NBS and EPA have identified several previously approved batches of CRMs as being of particular interest. The vendors were contacted with the request that one of the previously audited samples from each of these batches be sent to RTI. During the winter of 1983, nine samples were reanalyzed. The period of time between the audits and the long-term stability checks ranged from 11 months to 25 months. The results of these measurements are given in Table V. In general, these data suggest that no significant changes in the concentrations of the samples have occurred. The largest variation in concentration was 0.28 percent relative. One cannot make broad statements concerning the long-term stability of all CRMs based on measurements of a few; nevertheless, these data are encouraging and suggest that CRMs will remain stable during their certification periods. This stability enhances the credibility of CRMs as attractive substitutes for SRMs.

Conclusions

This paper has dealt with the performance audit program for CRMs and has presented a comparison of vendor and auditor results for 23 CRM batches approved for sale. In general, the agreement between the two sets of results has been within 0.5 percent relative. This comparison demonstrates that CRMs can be produced and analyzed by specialty gas vendors with a precision and accuracy approaching that of NBS-SRMs. Additional data presented concerning the long-term stability of CRMs suggest that CRMs are stable over their certification periods.

Acknowledgments

The performance audit program for Certified Reference Materials is supported by the U.S. Environmental Protection Agency under EPA Contract No. 68-02-3431. The authors acknowledge the advice and technical assistance of Ernest E. Hughes, George C. Rhoderick Walter R Miller, and William D. Dorko of the National Bureau of Standards.

References

1 Code of Federal Regulations, Title 40, Chapter I, Parts 50 and 58 (1980).

2 Code of Federal Regulations, Title 40, Chapter I, Part 86 (1980).

3 E. E. Hughes, "Development of Standard Reference Materials for air quality measurement," Advances in Instrumentation, 29 (Part 3):Paper 704, 13 pages (1974).

4 E. E. Hughes, "Certified Reference Materials for continuous emission monitoring," Journal of the Air Pollution Control Association, 32 (7):708-711 (1982).

5 E. E. Hughes and J. Mandel, A Procedure for Establishing Traceability of Gas Mixtures to Certain National Bureau of Standards Standard Reference Materials, Environmental Protection Agency Publication No. EPA-600/7-81-010, National Bureau of Standards Publication No. NBSIR 81-2227 (1981).

6 Environmental Protection Agency, "National ambient air quality measurement methodology; Ambient air quality surveillance," Federal Register, 48 (14):2528-2530 (January 20, 1983).

7 J. M, Marzen (EPA Office of Mobile Source Air Pollution Control), Letter to Paul J. Mann (Compressed Gas Association) (November 23, 1981).

8 EPA maintains a current list of batches of CRMs that have been approved for sale and of their vendors. A copy of this list may be obtained by calling Ms. Katherine A. Powers at (919) 541-2198, or by writing her at the following address: Quality Assurance Division (MD-77), Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

9 E. E. Hughes and J. E. Suddueth, "A computer-operated gas analysis system (COGAS) for the sequential analysis of multiple samples of compressed gas," unpublished manscript, National Bureau of Standards, Washington, DC.

Table I. Vendor's analytical results for a batch of 47.2 parts per million carbon monoxide in nitrogen CRMs.

Sample	First analysis concentration (ppm)	Second analysis concentration (ppm)	Difference (ppm)	Mean concentration (ppm)
1[a]	47.197[b]	47.206[c]	-0.009	47.202
2	47.149	47.239	-0.090	47.194
3	46.941	47.167	-0.226	47.054
4	47.197	47.144	+0.053	47.170
5	47.178	47.201	-0.023	47.190
6	47.244	47.169	+0.075	47.206
7	47.263	47.167	+0.096	47.215
8	47.150	47.255	-0.105	47.202
9	46.847	47.350	-0.503	47.098
10	47.055	47.308	-0.253	47.182
11	47.282	47.192	+0.090	47.237
Mean	47.137	47.218	-0.081	47.177
Std. dev.	0.137	0.064	0.184	0.054

[a] Internal standard for the batch.
[b] The standard deviation for 11 measurements of the internal standard during the first analysis was 0.076 ppm.
[c] The standard deviation for 9 measurements of the internal standard during the second analysis was 0.114 ppm.

Table II. Auditor's analytical results for two samples from a batch of 47.2 parts per million carbon monoxide in nitrogen CRMs.

Analysis number	Sample 5 concentration (ppm)	Sample 7 concentration (ppm)
1	47.275	47.278
2	47.281	47.281
3	47.271	47.266
4	47.266	47.294
5	47.289	47.310
6	47.270	47.289
7	47.275	47.288
8	47.293	47.310
9	47.276	47.278
10	47.269	47.267
Mean	47.276	47.286
Std. dev.	0.009	0.015

Table III. Comparison of Research Triangle Institute measured values with National Bureau of Standards certified values for "unknowns".

"Unknown" SRM composition	Nominal SRM concentration (ppm)	NBS certified value (ppm)	RTI measured value (ppm)	Agreement[a] (percent relative)
Carbon monoxide in nitrogen	50	44.9	44.77	- 0.29
	50	45.3	45.29	- 0.02
	100	93.6	93.88	+ 0.30
	250	243.7	243.66	- 0.02
	500	476.	475.85	- 0.03
	1000	956.	953.16	- 0.30
Nitric oxide in nitrogen	50	47.8	47.82	+ 0.04
	100	96.4	96.53	+ 0.13
	250	235.4	235.23	- 0.07
	500	462.0	461.61	- 0.08
	1000	957.	957.27	+ 0.03
Sulfur dioxide in nitrogen	50	44.95	44.70	- 0.56
	100	95.1	95.10	0.00
	3500	3122.	3138.2	+ 0.52

[a] $\text{Agreement} = 100 \left[\frac{\text{RTI measured value} - \text{NBS certified value}}{\text{NBS certified value}} \right]$.

Table IV. Comparison of Research Triangle Institute audit results with vendor analytical results for approved batches of CRMs.

CRM composition	Nominal CRM concentration	Vendor-measured value	Auditor-measured value	Agreement[a] (percent relative)
Carbon monoxide in nitrogen	10 ppm	9.91 ppm	9.94 ppm	+ 0.30[b]
		9.89 ppm	9.95 ppm	+ 0.61[b]
	25 ppm	24.28 ppm	24.21 ppm	- 0.29
		24.29 ppm	24.23 ppm	- 0.25
		24.32 ppm	24.27 ppm	- 0.21
		24.32 ppm	24.26 ppm	- 0.25
	50 ppm	48.39 ppm	48.49 ppm	+ 0.21
		48.42 ppm	48.50 ppm	+ 0.17
		47.16 ppm	47.20 ppm	+ 0.08
		47.20 ppm	47.21 ppm	+ 0.02
		47.19 ppm	47.28 ppm	+ 0.19
		47.22 ppm	47.29 ppm	+ 0.15
	100 ppm	97.12 ppm	96.85 ppm	- 0.28
		97.22 ppm	96.88 ppm	- 0.35
	250 ppm	243.9 ppm	243.9 ppm	0.00
		244.0 ppm	243.9 ppm	- 0.04
		244.1 ppm	244.2 ppm	+ 0.04
		244.0 ppm	244.2 ppm	+ 0.08
	500 ppm	472.5 ppm	473.0 ppm	+ 0.11
		472.9 ppm	472.9 ppm	0.00
		476.2 ppm	474.8 ppm	- 0.29
		476.1 ppm	474.8 ppm	- 0.27
	1000 ppm	946.4 ppm	944.6 ppm	- 0.19
		946.4 ppm	944.2 ppm	- 0.23
		969.8 ppm	971.8 ppm	+ 0.21
		970.0 ppm	971.0 ppm	+ 0.10
	2500 ppm	2404 ppm	2414 ppm	+ 0.42
		2406 ppm	2413 ppm	+ 0.29
		2406 ppm	2414 ppm	+ 0.33
		2404 ppm	2413 ppm	+ 0.37
	5000 ppm	4683 ppm	4690 ppm	+ 0.15
		4683 ppm	4692 ppm	+ 0.19
		4698 ppm	4716 ppm	+ 0.38[c]
		4702 ppm	4708 ppm	+ 0.13[c]

Table IV. (continued)

CRM composition	Nominal CRM concentration	Vendor Measured value	Auditor measured value	Agreement[a] (percent relative)
Carbon monoxide in nitrogen	8 %	7.71%	7.721%	+ 0.1
		7.71%	7.736%	+ 0.3
Carbon monoxide in air	43 ppm	42.36 ppm	42.40 ppm	+ 0.09
		42.30 ppm	42.45 ppm	+ 0.35
		42.70 ppm	42.70 ppm	0.00
		42.74 ppm	42.69 ppm	- 0.12
Nitric oxide in nitrogen	250 ppm	243.3 ppm	243.3 ppm	0.00
		243.7 ppm	243.3 ppm	- 0.16
		236.4 ppm	236.4 ppm	0.00
		236.4 ppm	235.9 ppm	- 0.21
	500 ppm	470 ppm	470.3 ppm	+ 0.1
		471 ppm	470.2 ppm	- 0.2

[a] $\text{Agreement} = 100 \left[\frac{\text{Auditor value} - \text{Vendor value}}{\text{Vendor value}} \right]$.

[b] Definitive analysis by NBS indicated that the carbon monoxide concentrations in these two samples are 9.94 ppm.

[c] Definitive analysis by NBS indicated that the carbon monoxide concentrations in these two samples are 4714 and 4710 ppm, respectively.

Table V. Data from long-term stability checks of CRMs

CRM composition	Nominal CRM concentration	Auditor analysis date	Auditor measured concentration	Change[a] (percent relative)
Carbon monoxide in nitrogen	50 ppm	January 1982	47.29 ppm	
		February 1983	47.34 ppm	+ 0.11
	50 ppm	January 1981	48.49 ppm	
		February 1983	48.61 ppm	+ 0.25
	50 ppm	January 1981	47.21 ppm	
		February 1983	47.31 ppm	+ 0.21
	250 ppm	August 1981	243.9 ppm	
		March 1983	244.2 ppm	+ 0.12
	250 ppm	January 1982	244.2 ppm	
		March 1983	244.2 ppm	0.00
	1000 ppm	January 1982	971.7 ppm	
		March 1983	971.3 ppm	- 0.04
	1000 ppm	January 1982	944.6 ppm	
		March 1983	947.2 ppm	+ 0.28
Carbon monoxide in air	43 ppm	January 1982	42.70 ppm	
		February 1983	42.77 ppm	+ 0.16
Nitric oxide in nitrogen	500 ppm	March 1982	470.2 ppm	
		February 1983	469.4 ppm	- 0.17

[a] $\text{Change} = 100 \left[\frac{\text{Second analysis concentration} - \text{First analysis concentration}}{\text{First analysis concentration}} \right]$

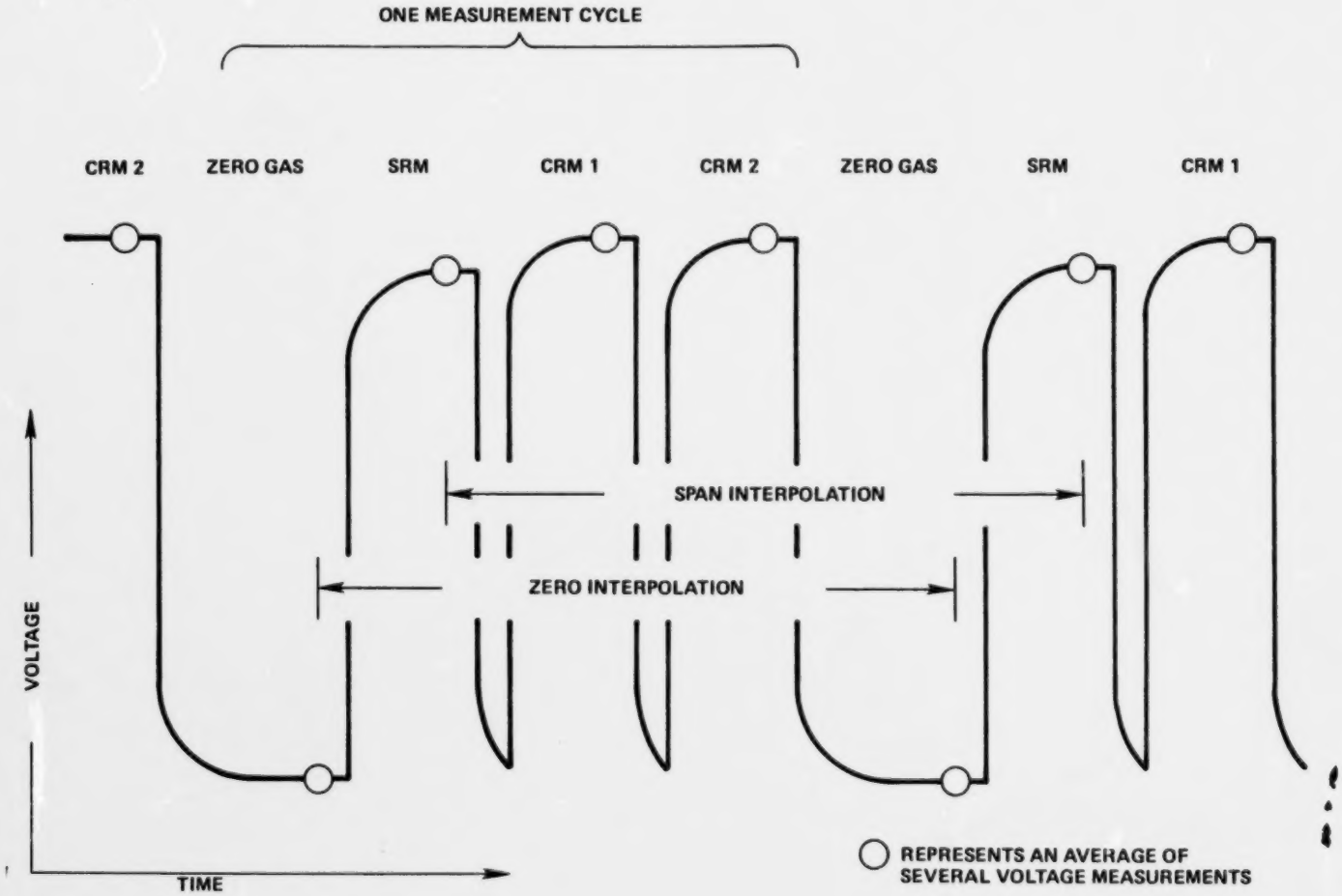


Figure 1. Stylized Representation of a Portion of a Strip Chart Trace from a Performance Audit of Certified Reference Materials

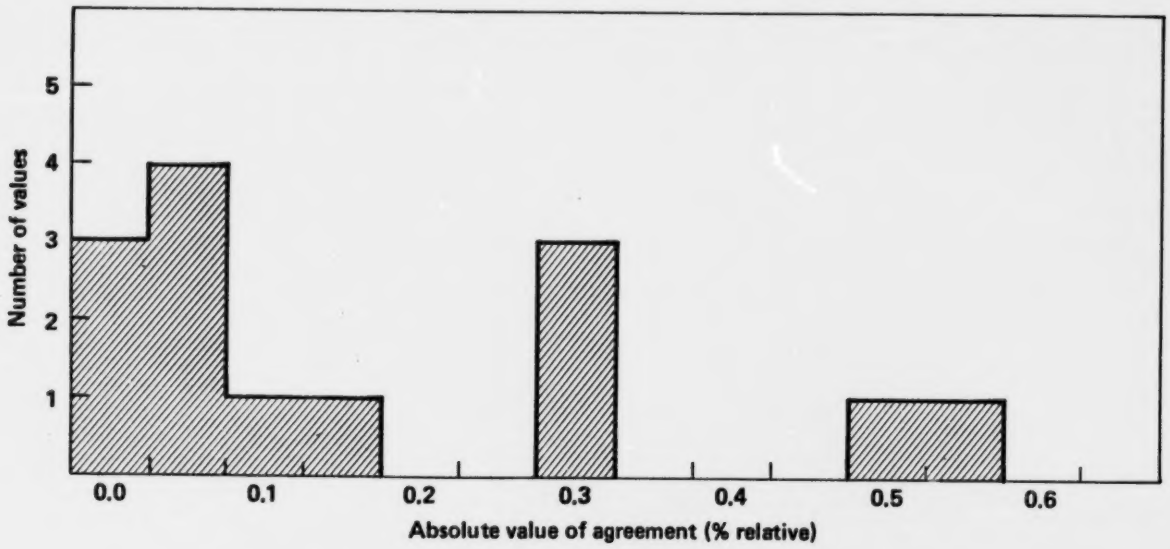


Figure 2. Frequency distribution for agreement between RTI measurements and NBS-certified values for "unknowns."

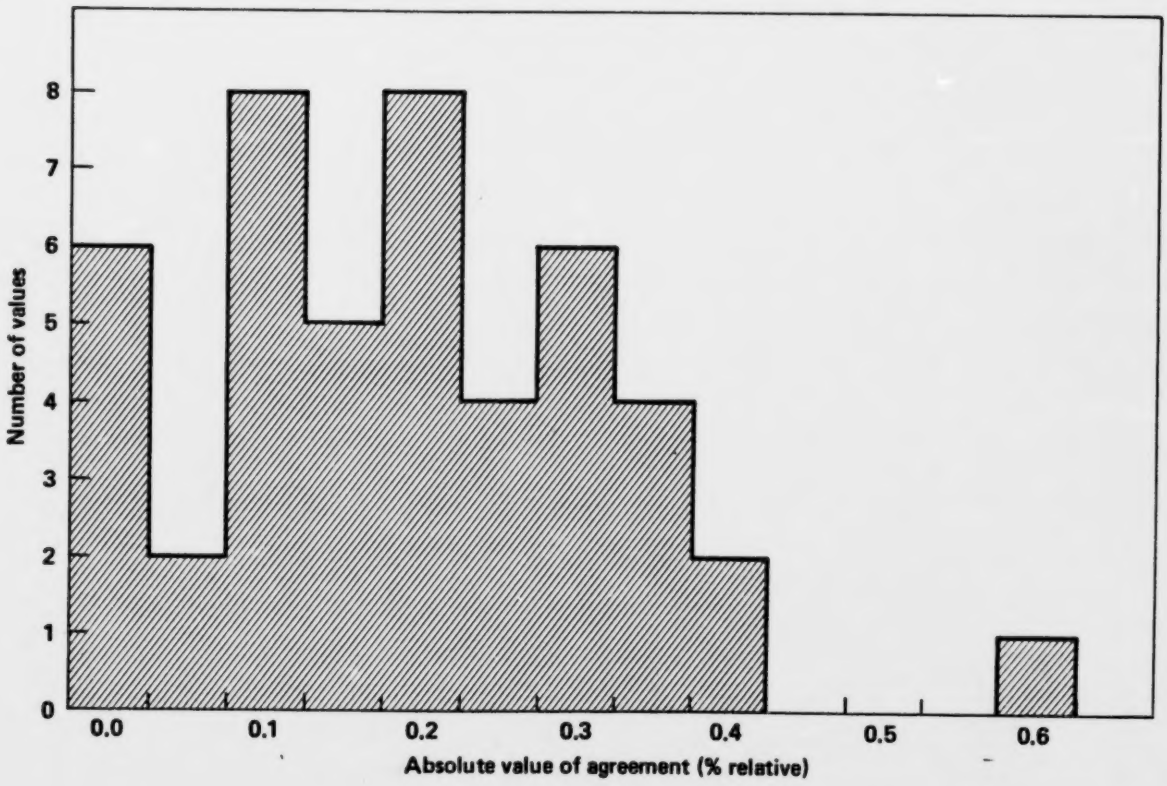


Figure 3. Frequency distribution for agreement between vendor and auditor analytical results for CRM batches.